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Notes:

1. Untranslatable words are replaced with asterisks (* **).
2. Texts in the figures are not translated and shown as it is.

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CLAIM + DETAILED DESCRIPTION

[Claim(s)]

[Claim 1] A transformer 1, the transformer 1 by which the content of four bindings is characterized by 500,000 or less and a molecular weight distribution (Mw/Mn) being [2.5-4, and crystal enthalpy-of-transition ΔH_{tr}] 70 - 150 J/g in more than 90 mol % and a weight average molecular weight (Mw), 4-polybutadiene.

[Claim 2] In a transformer 1 and 4 structure content, more than 90 mol % and a weight average molecular weight 500,000 or less The transformer 1, 4-polybutadiene which are characterized by completing generation of heat of 70 J/g in [temperature] 12-30 degrees C from phase change starting temperature in measurement of 70 - 150 J/g and uniform cooling of a differential scanning calorimeter of crystal enthalpy-of-transition ΔH_{tr} .

[Claim 3] (A) a vanadium compound and (B) R12AlX (the inside of a formula, and R1 -- the hydrocarbon group of carbon numbers 1-10 --) X shows halogen. The halogen content dialkyl aluminium compound expressed, (C) R21.5 AlX1.5 [and] (the inside of a formula, and R2 -- the hydrocarbon group of carbon numbers 1-10 --) X shows halogen. It consists of a halogen content sesquialkylaluminum compound expressed. (B) a component -- (-- C --) -- a component -- comparatively -- (-- B --) -- / -- [-- (-- B --) -- + -- (-- C --) --] (molar ratio) -- = -- 0.1 - 0.9 -- it is -- a catalyst -- using -- things -- the feature -- carrying out -- being according to claim 1 to 2 -- a transformer -- one -- four - polybutadiene -- manufacture -- a method .

[Claim 4] (A) a vanadium compound and (B) R12AlX (the inside of a formula, and R1 -- the hydrocarbon group of carbon numbers 1-10 --) X shows halogen. The halogen content dialkyl aluminium compound expressed, (C) R21.5AlX1.5 [and] (the inside of a formula, and R2 -- the hydrocarbon group of carbon numbers 1-10 --) X shows halogen. In the manufacture method of a transformer 1 and 4-polybutadiene using the catalyst which consists of a halogen content sesquialkylaluminum compound expressed (B) a component -- (-- C --) -- a component -- a rate -- (-- B --) -- / -- [-- (-- B --) -- + -- (-- C --) --] (molar ratio) -- = -- 0.1 - 0.9 -- the range --

changing -- things -- the feature -- carrying out -- a transformer -- one -- four - polybutadiene -- molecular weight -- adjusting -- a method .

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This inventions are the new transformers 1 and 4. - It is related with polybutadiene and its manufacture method.

[0002]

[Description of the Prior Art] It is known that the polymer in which polybutadiene has various microstructure according to a polymerization catalyst will be obtained. It is indicated in particular to JP,H9-124735,A, JP,H9-268208,A, JP,H9-272861,A, etc., The polybutadiene which makes a transformer 1 and 4-structures main structures polymerizes in the catalyst system which consists of a vanadium compound and an organometallic compound, and since generation polymer has the large latent heat by crystal transition, the application to the charge of a thermal storage medium etc. is expected.

[0003] In JP,H9-268208,A, it has specific structure, and application to the transformer 1 whose crystal enthalpy-of-transition change is 70 or more J/g, 4-polybutadiene, and a thermal storage medium is indicated. However, the transition velocity in the cooling process is not specifically indicated about generation of heat accompanying a phase change.

[0004]

[Problem(s) to be Solved by the Invention] This invention aims at offer of the new transformer 1 which has a molecular weight distribution large in comparison, 4-polybutadiene, its manufacture method, and the molecular weight regulation method.

[0005]

[Means for Solving the Problem] This invention relates to a transformer 1, the transformer 1 by which the content of four bindings is characterized by 500,000 or less and a molecular weight distribution (Mw/Mn) being [2.5-4, and crystal enthalpy-of-transition ΔH_{tr}] 70 - 150 J/g in more than 90 mol % and a weight average molecular weight (Mw), and 4-polybutadiene.

[0006] In a transformer 1 and 4 structure content, more than 90 mol % and a weight average molecular weight this invention 500,000 or less [moreover,] Crystal enthalpy-of-transition ΔH_{tr} is related with the transformer 1 and 4-polybutadiene which are characterized by completing generation of heat of 70 J/g in [temperature] 12-30 degrees C from phase change starting temperature in measurement of 70 - 150 J/g and uniform cooling of a differential scanning calorimeter.

[0007] Moreover, this inventions are the (A) vanadium compound and (B) R12AlX (among a formula). R1 The hydrocarbon group of carbon numbers 1-10 and X show halogen. The

halogen content dialkyl aluminium compound expressed, (C) R21.5AlX1.5 [and] (the inside of a formula, and R2 -- the hydrocarbon group of carbon numbers 1-10 --) X shows halogen. It consists of a halogen content sesquialkylaluminum compound expressed. (B) a component -- (C --) -- a component -- comparatively -- (B --) -- /- [(B --) -- + -- (C --) --] (molar ratio) -- = -- 0.1 - 0.9 -- it is -- a catalyst -- using -- things -- the feature -- carrying out -- the above -- a transformer -- one -- four - polybutadiene -- manufacture -- a method -- being related .

[0008] (A) a vanadium compound and (B) R12AlX (the inside of a formula, and R1 -- the hydrocarbon group of carbon numbers 1-10 --) X shows halogen. The halogen content dialkyl aluminium compound expressed, (C) R21.5AlX1.5 [and] (the inside of a formula, and R2 -- the hydrocarbon group of carbon numbers 1-10 --) X shows halogen. In the manufacture method of a transformer 1 and 4-polybutadiene using the catalyst which consists of a halogen content sesquialkylaluminum compound expressed (B) a component -- (C --) -- a component -- a rate -- (B --) -- /- [(B --) -- + -- (C --) --] (molar ratio) -- = -- 0.1 - 0.9 -- the range -- changing -- things -- the feature -- carrying out -- a transformer -- one -- four - polybutadiene -- molecular weight -- adjusting -- a method -- being related .

[0009]

[Embodiment of the Invention] The content of a transformer 1 and four bindings of a transformer 1 and 4-polybutadiene is 95% or more preferably 90% or more in the calculation from spectra, such as an IR spectrum or ¹H-NMR, and ¹³C-NMR.

[0010] Moreover, the crystal transition temperature from low-temperature crystal structure to high temperature crystal structure is 50-80 degrees C, and the transformer 1 of this invention and 4-polybutadiene can be changed by molecular weight, microstructure, etc.

[0011] Here, the fusing point and the crystal transition point were measured using the differential scanning calorimeter (DSC). After ****(ing) with a constant temperature first and making it dissolve completely at 200 degrees C under nitrogen-gas-atmosphere mind, it lowers the temperature and recrystallizes to 30 degrees C with a constant temperature, and **** to 200 degrees C again. Let the peak point of the peak which measures the differential heat at the time of the 2nd ****, and is equivalent to fusion, and the peak point of the peak equivalent to crystal transition be a fusing point and a crystal transition point.

[0012] The weight average molecular weight of the transformer 1 of this invention and 4-polybutadiene is 200,000 or less preferably 500,000 or less. Moreover, a number average molecular weight is desirable and the transformer 1 of this invention and 4-polybutadiene are 100,000 or less especially preferably 200,000 or less.

[0013] A fusing point is desirable and the transformer 1 of this invention and 80-140 degrees C of 4-polybutadienes are 80-130 degrees C especially preferably. Since it is low temperature comparatively, shaping processing to a lamination with a pellet, sheet metal, and a metal plate,

a hollow filament, a structure, a cast film, etc. is possible. Moreover, it is small in the solubility of glycols, such as silicon oil and ethylene glycol, and they can be used as a heat carrier. Furthermore, prolonged continuous use can be carried out in nitrogen sealing atmosphere.

[0014] The transformer 1 of this invention and 4-polybutadiene are desirable, and molecular weight distributions (M_w/M_n) are 2.5-4.

[0015] 70-150J /of crystal enthalpy-of-transition $\Delta H_{tr}(s)$ of the transformer 1 of this invention and 4-polybutadiene are [g] 90 - 140 J/g preferably.

[0016] In measurement of uniform cooling of a differential scanning calorimeter, 70J/g generation of heat ends the transformer 1 of this invention, and 4-polybutadiene in [temperature] 12-30 degrees C from phase change starting temperature.

[0017] [the transformer 1 of this invention, and 4-polybutadiene] (A) a vanadium compound and (B) R12AIX (the inside of a formula, and R1 -- the hydrocarbon group of carbon numbers 1-10 --) X shows halogen. The halogen content dialkyl aluminium compound expressed, (C) R21.5AIX1.5 [and] (the inside of a formula, and R2 -- the hydrocarbon group of carbon numbers 1-10 --) X shows halogen. expressing -- having -- halogen -- content -- sesquione -- alkylaluminum -- a compound -- from -- becoming -- a catalyst -- it is -- (-- B --) -- a component -- (-- C --) -- a component -- comparatively -- (-- B --) -- /- [-- (-- B --) -- + -- (-- C --) --] (molar ratio) -- = 0.1 - 0.9 -- it is -- a catalyst system -- using -- it can manufacture .

[0018] As a (A) vanadium compound of a catalyst system, vanadium thoria cetyl acetato, a vanadium trichloride THF complex, vanadium trichloride oxide, naphthenic acid vanadium, etc. can be mentioned.

[0019] The (B) component of a catalyst system is a halogen content dialkyl aluminium compound expressed with R12AIX (R1 shows the hydrocarbon group of carbon numbers 1-10 among a formula, and X shows halogen.). R1 It is the hydrocarbon group of carbon numbers 1-10, and a methyl group, an ethyl group, butyl, a HEKICHIRU machine, an octyl group, etc. are mentioned. X is halogen and chlorine, bromine, etc. are mentioned. As a concrete compound of R12AIX, dimethyl aluminium chloride, Diethyl aluminium chloride, dibutyl aluminium chloride, dioctyl aluminium chloride, a dimethyl aluminium star's picture, a diethyl aluminium star's picture, etc. can be mentioned.

[0020] The (C) component of a catalyst system is a halogen content sesquialkylaluminum compound expressed with R21.5AIX1.5 (R2 shows the hydrocarbon group of carbon numbers 1-10 among a formula, and X shows halogen.). R2 It is the hydrocarbon group of carbon numbers 1-10, and a methyl group, an ethyl group, butyl, a HEKICHIRU machine, an octyl group, etc. are mentioned. X is halogen and chlorine, bromine, etc. are mentioned. R21.5AIX1.5 as a concrete compound Sesquimethyl aluminium chloride, sesquiethyl aluminium chloride, sesquibutyl aluminium chloride, sesquiocetyl aluminium chloride, a sesquimethyl aluminium star's picture, a sesquiethyl aluminium star's picture, etc. are

mentioned.

[0021] this invention -- it is -- if -- (-- B --) -- a component -- (-- C --) -- a component -- comparatively -- (-- B --) -- /- [- (-- B --) -- + -- (-- C --) -] (molar ratio) -- = -- 0.1 - zero . -- nine -- it is 0.15-0.7 preferably.

[0022] Restriction in particular does not have a polymerization method and it can apply block polymerization, solution polymerization, etc. As a solvent in solution polymerization, aromatic series system hydrocarbons, such as toluene, benzene, and xylene, Aliphatic hydrocarbon, such as n-hexane, butane, heptane, and pentane, cyclopentane, Alicyclic hydrocarbon, such as cyclohexane, 1-butene, ****- 2 - Butene, transformer 2 - Hydrocarbon system solvents, such as olefin hydrocarbon, such as butene, a mineral spirit, solvent naphtha, and kerosene, halogenated hydrocarbon system solvents, such as a methylene chloride, etc. are mentioned. Moreover, it is good also considering 1,3-butadiene itself as a polymerization solvent.

[0023] in each polymerization method -- polymerization time -- 5 minutes - 12 hours -- desirable -- 5 minutes - 2 hours, and polymerization temperature -20-100 degrees C can be preferably performed at 0-60 degrees C.

[0024] Especially in this invention, although not limited, butadiene can be polymerized by the aforementioned catalyst system. However, in the range which does not spoil polymer physical properties, you may perform copolymerization with a small amount of different-species olefin, conjugated diene, or nonconjugated diene. As olefin, ethylene, propylene, butene-1, 4-methyl pentene 1, hexene 1, octene 1, norbornene, cyclopentene, bird methylvinyl silane, etc. are mentioned. As conjugated diene, isoprene, 2, 3-dimethylbutadiene, 1,3-pentadiene, 2-methyl 1,3-pentadiene, 4-methyl 1,3-pentadiene, 2, and 4-hexadiene etc. is mentioned. As nonconjugated diene, dicyclopentadiene, 5-ethylidene 2-norbornene or 1, and 5-hexadiene etc. is mentioned.

[0025] [the transformer 1 of this invention, and 4-polybutadiene] An amine ketone system, an aromatic series secondary amine system, a mono-phenol system, a bisphenol system, A polyphenol system vent imidazole system, a dithiocarbamic acid system, a thiourea system, The stability of polymer and a life can be developed by carrying out about 0.01 to 4 phr addition of anti-oxidants, such as a phosphorous acid system, an organic thio acid system, a special wax system, and two or more kinds of mixed systems, light stabilizer, the thermostabilizer, etc. These are tris (nonyl phenyl) phosphite, 2, and 6-G tert-butyl 4-methyl phenol etc., for example.

[0026]

[Example] It computed with "the content of a transformer 1 and four bindings" from the IR spectrum for which it asked with the KBR tablet method using JEOL diffraction grating infrared spectrophotometer (FT-IR) JIR-5500. That is, it asked for each rate of transformers 1 and 4, ****- 1 and 4, and vinyl binding by calculation from the peak of 966cm⁻¹ or 730cm⁻¹ or 912cm⁻¹

1.

[0027] It asked for the "fusing point" and the "crystal transition point" as follows. Using the differential scanning calorimeter (DSC) of SSC5200 by SEIKO electronic industry incorporated company, under nitrogen-gas-atmosphere mind, first, what paid and carried out Shilu of 10mg of the samples to the sample bread made from aluminum is ****(ed) by a part for 10-degree-C/, and is heated 250 degrees C from a room temperature for 10 minutes. After making it dissolve completely, by a part for -5-degree-C/, the temperature was lowered to -30 degrees C, and it held for 10 minutes, and ****(ed) to 200 degrees C by a part for 10-degree-C/again.

Temperature of the peak which measures the differential heat at the time of the 2nd ****, and is equivalent to fusion, and temperature of the peak equivalent to crystal transition were made into the "fusing point" and the "crystal transition point", respectively.

[0028] A weight average molecular weight and a number average molecular weight use styrene as a standard substance, and ask for it by a gel permeation chromatography (GPC), using o-dichlorobenzene as a solvent.

[0029] (Work example 1) They are heptane 84ml and butadiene 16ml to the flask which fully carried out nitrogen displacement. After adding, (A) vanadium thoria cetyl acetonoato (V (AA) 3) 0.1mmol, (B) diethyl aluminium chloride (DEAC) 2mmol, and (C) ethylaluminumsesquichloride (EASC) 8mmol were added one by one, and the polymerization was started. The polymerization was performed for 5 minutes at 20 degrees C under nitrogen-gas-atmosphere mind. 2%HCl/Etah Nor r300ml was added, the polymer was settled, and it collected.

Conditions and a result were collectively shown in Tables 1-2.

[0030] (Work examples 2-10) (comparative examples 1-2)

Except having carried out on the conditions shown in Table 1, it polymerized like the work example 1 and transformer 1.4-polybutadiene was obtained. The result was summarized in Table 2.

[0031]

[Table 1]

実施例 No.	(B)DEAO mmol	(C)EASO mmol	(B)/(B)-(C)	収量 g	収率 g/mmol	生産性 g/mmol·hr
1	2	8	0.2	2.08	20.8	249
2	4	6	0.4	1.84	18.4	221
3	8	2	0.8	1.18	11.8	142
4	9	1	0.9	0.68	6.8	82
5	2	4	0.33	1.58	15.8	189
6	2	6	0.25	1.74	17.4	208
7	2	8	0.2	2.08	20.8	249
8	2	8	0.2	1.82	18.2	218
9	2	10	0.17	1.89	18.9	227
10	2	15	0.12	1.64	16.4	197
比較例						
1	0	10	0	1.05	10.5	126
2	10	0	1	trace	trace	0

[0032]

[Table 2]

実施例 No.	相転移開始 温度(°C)	結晶転移 エンタルピー ΔH_{tr} (J/g)	融点 Mp(°C)	重量平均 分子量(Mw)	数平均分子 量(Mn)	Mw/Mn
1	58.9	71.9	100.7	127,000	44,000	2.88
2	57.8	74.6	104.3	104,000	39,000	2.68
3	64.1	108	115	67,000	27,000	2.45
4	70.1	103.8	125.1	16,000	7,000	2.34
5	58.7	83.7	103.9	118,000	37,000	3.17
6	57.3	80.6	103.4	98,000	34,000	2.91
7	56.9	71.9	100.7	127,000	44,000	2.88
8	55.1	57.9	92.2	104,000	38,000	2.73
9	58.2	80.6	103.4	85,000	39,000	2.2
10	57.3	79.7	102.9	87,000	29,000	2.95
比較例						
1	58.5	68.2	98.4	55,000	32,000	1.75
2	—	—	—	—	—	—

[0033]

[Effect of the Invention] The method of controlling the new transformer 1 which has a molecular weight distribution large in comparison, 4-polybutadiene, its manufacture method, and molecular weight can be offered.

[Translation done.]